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## PATENT ABSTRACTS OF JAPAN

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(71)Applicant : NIKKO KYODO CO LTD

(22)Date of filing : 24.04.1991

(72)Inventor : SO HIDEHIKO  
TSUJI MASAHIRO

## (54) COPPER ALLOY FOR CONDUCTIVE SPRING

## (57)Abstract:

PURPOSE: To obtain a copper alloy having high strength and high conductivity and excellent in stress relaxation property, thermal peeling resistance of plating, silver plating suitability, and stress corrosion cracking resistance.

CONSTITUTION: The alloy is an alloy which has a composition containing 0.5-4.0% Ni, 0.1-1.0% Si, 0.01-0.1% Mg,  $\leq 0.0015\%$  S, and  $\leq 0.0015\%$  O or further containing, as accessory components, 0.005-1.0% of one or  $\geq 2$  elements among P, B, As, Fe, Co, Cr, Al, Sn, Ti, Zr, In, and Mn and further an alloy which has a composition containing, besides the above components, 0.01-15% Zn. This alloy can be used for terminal, connector, relay, switch, etc.

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CLAIMS

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## [Claim(s)]

[Claim 1] nickel: The copper alloy for conductive springs characterized by the bird clapper from Remainder Cu 0.5-4.0% (it is below the same% of the weight), Si:0.1-1.0%, Mg:0.01-0.1%, S:0.0015% or less, and O:0.0015% or less.

[Claim 2] nickel: The copper alloy for conductive springs characterized by the bird clapper from Remainder Cu 0.5-4.0%, Si:0.1-1.0%, Mg:0.01-0.1%, Zn:0.01-15%, S:0.0015% or less, and O:0.0015% or less.

[Claim 3] nickel: 0.5-4.0%, Si:0.1-1.0%, and Mg: — the copper alloy for conductive springs which contains one sort or two sorts or more 0.005 to 1.0% as an accessory constituent further among P, B, As, Fe, Co, Cr, aluminum, Sn, Ti, Zr, In, and Mn, and is characterized by the bird clapper from Remainder Cu O:0.0015% or less S:0.0015% or less 0.01 to 0.1%

[Claim 4] nickel: 0.5-4.0%, Si:0.1-1.0%, Mg:0.01-0.1%, Zn: 0.01-15%, S:0.0015% or less, O:0.0015% or less, The copper alloy for conductive springs which furthermore contains one sort or two sorts or more 0.005 to 1.0% as an accessory constituent among P, B, As, Fe, Co, Cr, aluminum, Sn, Ti, Zr, In, and Mn, and is characterized by the bird clapper from Remainder Cu.

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DETAILED DESCRIPTION

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[Detailed Description of the Invention]

[0001]

[Industrial Application] this invention relates to the copper alloy for conductive springs used for a terminal, a connector, a relay, a switch, etc.

[0002]

[Description of the Prior Art] Conventionally, as a copper alloy for these springs, brass and phosphor bronze are used widely and titanium copper and the beryllium copper were used for what high intensity is required as in part.

[0003]

[Problem(s) to be Solved by the Invention] In recent years, what has high intensity and a high spring property is called for by the miniaturization of a device and parts, and a good material of a stress relaxation characteristic is especially called for from a viewpoint of the long-term reliability of a spring property. Moreover, since it is necessary to prevent the temperature rise of the parts at the time of use as much as possible to make a stress relaxation characteristic good, material with high electrical conductivity is called for good [ thermolysis nature ].

[0004] The heat-resistant detachability of Sn plating and solder plating is still better, and high-reliability material without the migration phenomenon under existence of moisture is called for. To such demand characteristics, although brass is a low cost, it is inferior to intensity and spring nature, and stress corrosion crack sensitivity is also high. Moreover, phosphor bronze and titanium copper had low electrical conductivity, and the beryllium copper is expensive and had merits and demerits, respectively.

[0005] Then, although the alloy of recent years many is shown, since the Cu-nickel-Si system alloy is excellent also with intensity and conductivity also in it, it is observed. Since a stress relaxation characteristic will be further improved if Mg is added as shown especially in USP4594221 (JP,61-250134,A), it is a material suitable as spring material. However, it turns out that the heat-resistant detachability of plating deteriorates remarkably when this alloy adds Mg, and the improvement was called for.

[0006]

[Means for Solving the Problem] As a result of inquiring about a Cu-nickel-Si-Mg system alloy in view of this situation, it came to obtain the alloy with which it is satisfied of many properties of all as spring material.

[0007] this invention Namely, nickel:0.5-4.0%, Si:0.1-1.0%, Mg: 0.01-0.1%, S:0.0015% or less, O:0.0015% or less. To the copper alloy or the above which consists of the remainder Cu, further P, B, As, Fe, They are the copper alloy which contains one sort or two sorts or more 0.005 to 1.0% among Co, Cr, aluminum, Sn, Ti, Zr, In, and Mn, and the alloy for conductive springs further contained Zn:0.01 to 15% into both the above-mentioned alloys, respectively.

[0008] Each reason for component limitation of this invention alloy is shown below. Although nickel generates Si and an intermetallic compound by the aging treatment and the reasons for making nickel content into 0.5 - 4.0% are intensity and a principal component which raises both conductivity, when intensity is low and exceeds 4.0%, they are for processability to fall at less than 0.5%.

[0009] although Si is effective in raising the migration-proof nature other than the effect which raises intensity, without seldom lowering conductivity with nickel, if the reason for making the content into 0.1 - 1.0% does not have those effects at less than 0.1% and exceeds 1.0%, conductivity will fall remarkably -- it is a sake

[0010] Although Mg raises a stress relaxation characteristic, it is a component which degrades the heat-resistant detachability of plating, and when it cannot improve a stress relaxation characteristic even if the reason for making Mg content into 0.01 - 0.1% specifies S and O, but it exceeds 0.1%, it is for the heat-resistant detachability of plating to fall at less than 0.01%.

[0011] The reason for making S content into 0.0015% or less In order to also make a stress relaxation characteristic good further, making Mg content low and improving the heat-resistant detachability of plating If it is because it turns out that S content does very important influence and S exists exceeding 0.0015% It is for Mg to serve as a sulfide so much and to distribute in material, to permeate, if a stress relaxation characteristic is not not only improved, but a plating article is heated while the heat-resistant detachability of plating deteriorates, even if Mg content is low, and for the defect of a blister to come to occur. The reason for making O content into 0.0015% or less is also to permeate, if a plating article is heated while a stress relaxation characteristic is not not only improving, but being completely the same as that of S, Mg's serving as an oxide and the heat-resistant detachability of plating deteriorating, and for the defect of a blister to occur.

[0012] That is, even if it begins by making both the contents of S and O into 0.0015% or less and makes Mg content low, the stress relaxation characteristic has been improved and the heat-resistant detachability of plating can be improved by making it low.

[0013] It became clear that a convention of the content of S and O is a key point for still a small amount of Mg to also prevent the heat-resistant detachability of plating and the stain of plating, and a blister.

[0014] Although addition of an accessory constituent improves intensity, the reason for making the content of the accessory constituent of P, B, and others into 0.005 - 1.0% is for conductivity to fall remarkably at less than 0.005% while processability will fall, if the effect does not exist and it exceeds 1.0%.

[0015] Although its migration-proof nature improves and it also reduces cost while its heat-resistant detachability of plating improves by adding Zn, when the reason for making Zn content into 0.01 - 15% does not have the effect and it exceeds 15%, it is

because stress corrosion crack sensitivity becomes high rapidly at less than 0.01%.

[0016]

[Example] Next, an example and the example of comparison are explained. Table 1 is component composition of the copper alloy which examined. Dissolution casting of the copper alloy of these composition was carried out in the atmosphere, and the ingot of the size of 30mmx60mmx120mm was obtained. After carrying out 3mm facing of these ingots of one side and removing surface discontinuity mechanically, the thickness of 6mm was made with rolling between 2-hour heating post heating at the temperature of 800-950 degrees C. After carrying out pickling and removing a surface scale, it cold-rolled by Mr. Atsushi of 0.5mm. Water quenching after solution treatment was performed for 5 - 10 minutes at the temperature of 800-900 degrees C after that. In addition, the grain size number after this solution treatment was adjusted to 10 micrometers. And after finishing cold-rolling to 0.3mm, it carried out on the conditions from which the maximum intensity is obtained in the aging treatment of 1 - 7 hours at the temperature of 400-500 degrees C, and surface polish was carried out with #1200 emery paper, and the last removed the surface discontinuity of a scale etc. and was taken as the test specimen.

[0017]

[Table 1]

		化 学 組 成 (重量%)							
		Cu	N i	S i	M g	S	O	Z n	副成分
本 発 明 合 金	1	残	2.25	0.55	0.026	0.0008	0.0007	—	—
	2	残	3.67	0.97	0.047	0.0010	0.0008	—	Co : 0.23
	3	残	1.87	0.43	0.028	0.0010	0.0014	—	Cr : 0.12, Zr : 0.09
	4	残	2.71	0.60	0.098	0.0004	0.0007	—	Ti : 0.27, Al : 0.65
	5	残	3.50	0.80	0.049	0.0012	0.0012	—	Sn : 0.35, P : 0.007
	6	残	0.84	0.19	0.050	0.0012	0.0014	7.30	B : 0.008, Al : 0.60
	7	残	3.62	0.93	0.049	0.0011	0.0005	0.92	—
	8	残	1.41	0.35	0.085	0.0010	0.0013	9.80	Fe : 0.34, Ti : 0.06
	9	残	2.85	0.75	0.067	0.0008	0.0006	1.82	—
	10	残	2.51	0.61	0.038	0.0011	0.0013	0.37	In : 0.08, As : 0.007
	11	残	1.29	0.33	0.022	0.0005	0.0009	3.16	Mn : 0.51

比 較 合 金	12	残	5.38	0.86	0.054	0.0007	0.0009	—	—
	13	残	3.10	1.13	0.092	0.0073	0.0013	1.54	—
	14	残	3.19	0.75	0.003	0.0005	0.0005	18.9	Sn : 0.53, P : 0.024
	15	残	2.54	0.68	0.33	0.0006	0.0012	5.10	—
	16	残	0.38	0.12	0.015	0.0009	0.0026	—	Cr : 0.13
	17	残	0.44	0.38	0.46	0.0012	0.0014	—	Fe : 0.16, P : 0.031
	18	残	1.96	0.45	0.051	0.0025	0.0013	26.8	—
	19	残	2.89	0.69	—	0.0011	0.0014	7.43	—
	20	残	1.93	0.52	0.038	0.0032	0.0019	1.15	Sn : 2.32
	21	残	1.40	0.08	0.076	0.0006	0.0008	1.42	—

[0018] Tensile strength, elongation, conductivity, a stress relaxation characteristic, tinning heatproof detachability, silver plating nature, and stress-corrosion-cracking-proof nature were examined about the test specimen. Tensile strength and elongation measured by performing a tension test using the JIS13B test piece for tensile test. Conductivity measured electric resistance at 20 degrees C by the four probe method after processing to the 10mmwx100ml test piece, and converted it into conductivity. a stress relaxation characteristic -- drawing 1 -- like -- ten -- mmw(s) -- x -- 100 -- mml -- having processed it -- board thickness -- 0.3 -- mm -- a test piece -- the gage length -- l -- = -- 50 -- mm -- height -- y -- zero -- = -- 20 -- mm -- bending stress -- a load -- carrying out -- 150 -- degree C -- 1000 -- an hour -- heating -- the back -- drawing 2 -- being shown -- permanent deformation -- an amount (height) -- y -- measuring -- stress relaxation -- a rate -- [ -- After tinning heatproof detachability performs 0.5-0.8-micrometer copper ground plating to a test specimen, Predetermined-time (every 100 hours) heating is carried out at 150 degrees C after cutting to 10mmwx100mml about the thing which electroplated 1-1.5-micrometer tin and which carried out afterbaking reflow processing. 90-degree bending of one side was performed one round trip by 0.3mm (= board thickness) of bend radii, it observed near the bending section on the rear face of front with the visual field of being 20 times many as this, and the existence of plating exfoliation was checked. Silver plating nature measured [ what / performed 1 micrometer of silver plating to the test specimen by making copper flash plate plating into a ground ] the number of blisters about the field of 2 (7mm\*\*x30 piece) 1470mm after heating for 2 minutes at 450 degrees C. Fixing the test specimen processed into 12.5mmwx150mml in the shape of a loop, indoors, after 12-hour neglect, stress-corrosion-cracking-proof nature was left in the desiccator with a capacity of 10l. which contains 2l. of aqueous ammonia 14%, broke visually, investigated the existence of generating, and evaluated it in time to crack generating. Migration-proof nature processed the test specimen into 10mmwx100mml, set it by 2 sets [ 1 ] like drawing 3, and was immersed into tap water (300ml) like drawing 4. Next, the direct current voltage of 14V was impressed between the test specimens of these two sheets, and change of the current value to elapsed time was measured. The example of representation of this result is shown in drawing 5. And evaluation of migration-proof nature was performed in time (the drawing 5 Nakaya mark) until current value is set to 1.0A. These evaluation results are shown in Table 2.

[0019]

[Table 2]

		引張強 さ(N/ mm <sup>2</sup> )	伸び (%)	導電 率(%) IACS	応力 緩和 率(%)	錫めっ き耐熱 剥離性 (hr)	銀めっき 性(ふく れの数)	耐応力 腐食割 れ性 (hr)	耐マイグ レーショ ン性 (min)
比較 合金	1	683	7.9	49	16	600	0	> 500	530
	2	741	5.3	41	15	500	0	> 500	700
	3	675	8.9	49	16	700	0	> 500	500
	4	717	6.3	42	10	600	0	> 500	570
	5	724	5.2	37	15	500	0	> 500	620
	6	534	13.3	40	16	>1000	0	400	420
	7	716	6.5	45	14	>1000	0	> 500	720
	8	642	5.2	42	13	>1000	0	400	600
	9	698	8.4	43	14	>1000	0	> 500	640
	10	698	7.8	45	16	>1000	0	> 500	570
	11	611	11.1	42	17	>1000	0	> 500	500
比較 合金	12	836	2.1	39	15	>1000	0	> 500	680
	13	704	6.6	29	21	100	67	> 500	830
	14	735	4.4	23	24	>1000	0	50	790
	15	691	4.6	41	9	100	0	400	690
	16	454	17.6	60	22	300	4	> 500	350
	17	643	10.2	53	10	100	0	> 500	470
	18	657	9.3	19	21	>1000	3	10	800
	19	698	6.1	43	23	>1000	0	> 500	670
	20	729	5.9	37	24	400	10	> 500	520
	21	480	22.8	52	11	>1000	0	> 500	200

[0020] It turns out that this invention alloy has good intensity and conductivity from this table, a stress relaxation characteristic is also good, and surface quality, such as tinning heatproof detachability and silver plating nature, is also very good, and stress-corrosion-cracking-proof nature is also good.

[0021] It is contrary to these, and about a comparison alloy, since No.12 have the high amount of nickel, although intensity is high, its elongation is low, and its processability is not so good. Since No.13 have the amount of Si, and the high amount of S, conductivity is low, a stress relaxation characteristic is also bad and surface quality, such as tinning heatproof detachability and silver plating nature, is bad. No.14 have the low amount of Mg, although it is an example with many amounts of Zn, for a low reason, the amount of Mg of a stress relaxation characteristic is not so good, since there are many amounts of Zn, conductivity is low, and stress-corrosion-cracking-proof nature is also bad. No. -- although 15 and 17 are examples with many amounts of Mg, and the stress relaxation characteristic is good, tinning heatproof detachability is bad. Since the amount of nickel is low and No.16 have zero (oxygen) high amount, sufficient intensity is not obtained but a stress relaxation characteristic, tinning heatproof detachability, and its silver plating nature are bad.

[0022] Since No.18 have many amounts of S, and amounts of Zn, a stress relaxation characteristic, silver plating nature, and its stress-corrosion-cracking-proof nature are bad. Although No.19 are the example which does not add Mg, its a stress relaxation characteristic is not so good.

[0023] Since No.20 have O and the high amount of S, a stress relaxation characteristic, tinning heatproof detachability, and its silver plating nature are bad. Since No.21 have few amounts of Si, sufficient intensity is not obtained but its migration-proof nature is also bad.

[0024] As explained above, this invention alloy O of a Cu-nickel-Si-Mg system alloy, Moreover, a stress relaxation characteristic is also good at high intensity and high electric conduction by specifying the amount of S, adding Zn and adding one sort or two sorts or more in P, B, As, Fe, Co, Cr, aluminum, Sn, Ti, Zr, In, and Mn further. Plating heatproof detachability and silver plating nature are also good, and stress-corrosion-cracking-proof nature is also good.

[0025]

[Effect of the Invention] this invention alloy is a copper alloy with good stress relaxation characteristic, plating heatproof detachability, silver plating nature, and stress-corrosion-cracking-proof nature in high intensity and high electric conduction, and a connector, a relay, a switch, etc. are the copper alloys which should be widely used in an electronic-parts field.

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DESCRIPTION OF DRAWINGS

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[Brief Description of the Drawings]

[Drawing 1] It is explanatory drawing of the stress relaxation characteristic examining method.

[Drawing 2] It is explanatory drawing about the amount of permanent deformation of a stress relaxation characteristic examination.

[Drawing 3] It is explanatory drawing of a migration-proof sex-test test specimen.

[Drawing 4] It is explanatory drawing of the migration-proof sex test.

[Drawing 5] It is the graph which shows the current-value field change to the elapsed time in the migration-proof sex test.

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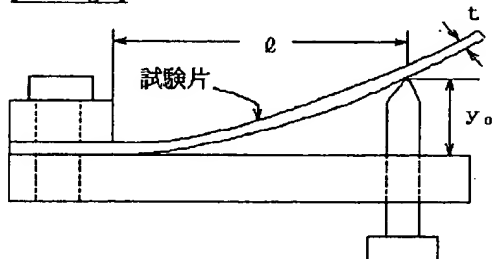
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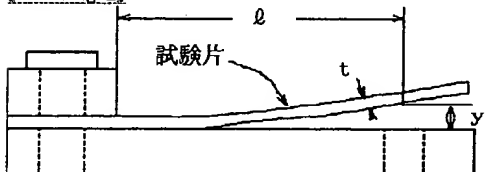
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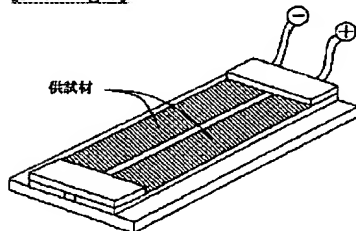
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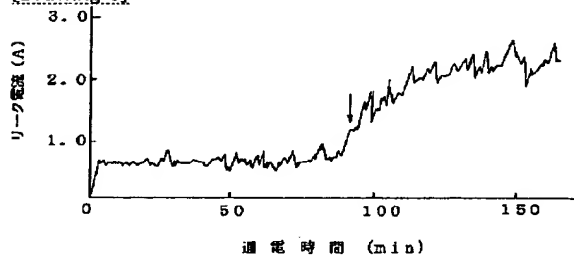
[Drawing 2]



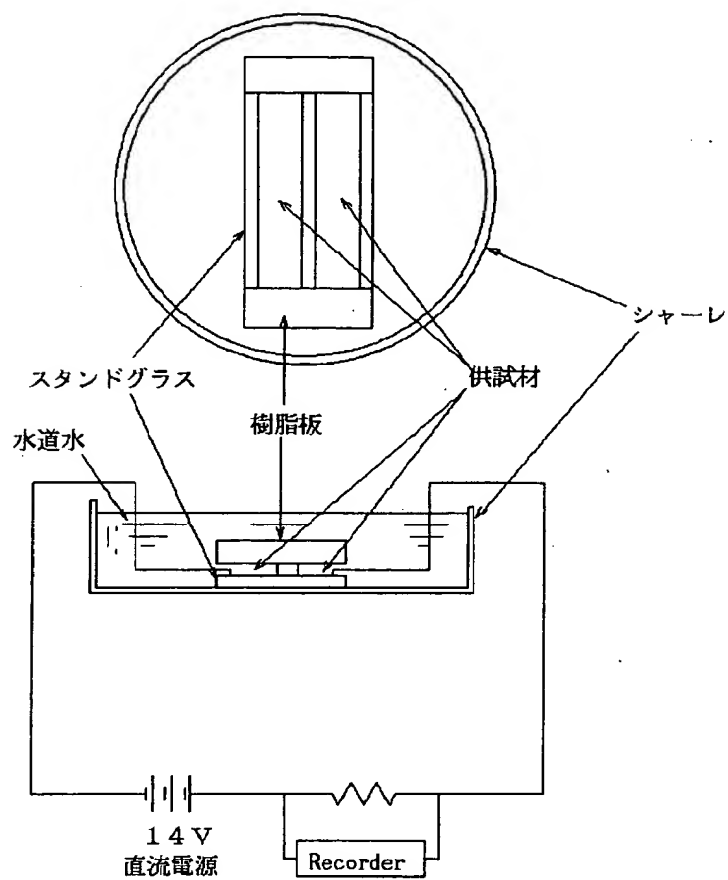
[Drawing 3]



[Drawing 5]



[Drawing 4]



[Translation done.]